Electrochemical Preparation of Semiconducting and Magnetic Metal Oxide Films

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Introduction

Preparation of oxide films from aqueous solutions has been considerable attention in several industries and has several advantages over other techniques such as sputtering, molecular beam epitaxy, chemical vapor deposition, and sol-gel technique.

The author has proposed a chemical process for preparing oxide films by using a nitrate-nitrite reaction in an aqueous solution and has demonstrated the preparation of zinc oxide(ZnO),[1-5] indium oxide,[6] cerium oxide,[7] and magnetite(Fe_3O_4) films.[8] The tentative chemical deposition mechanism of metal(M) oxide films from aqueous solutions containing the nitrate salts and dimethylamineborane (DMAB) was described by the following schemes:

$$M(NO_3)_n \longrightarrow M^{n+} + nNO_3^- \quad (1)$$

$$(CH_3)_2NHBH_3+2H_2O \rightarrow BO_2^-+(CH_3)_2NH +7H^++6e^- \quad (2)$$

$$NO_3^- + H_2O +2e \longrightarrow NO_2^- + 2OH^- \quad (3)$$

$$M^{n+} + nOH^- \longrightarrow M(OH)_n \longrightarrow MO_{n/2} + (n/2)H_2O \quad (4)$$

The reduction reaction of the nitrate ion(3) plays an important role in oxide film formation from the solution and is driven with an oxidation reaction of DMAB(2) contained in the solution.

Preparation of ZnO film and its applications

ZnO film was prepared only by immersing substrates into aqueous solution containing zinc nitrate hydrous and DMAB at 333K. Glasses, polymers, and metal sheets were used as the substrate. Prior to the preparation, the substrate was activated with an industrially employed Pd/Sn two-step catalytic activation process.

The deposition rate strongly depended on the preparation parameters of solution temperature, and concentrations of the nitrate salt and DMAB.

ZnO film had characteristic wurtzite structure and optical band gap energy of 3.3eV, irrespective of preparation conditions. The resistivity ranging from $8x10^{-4}$ to $2x10^{8}\Omega$cm could be obtained by incorporating small amounts of impurities such as In^{3+} and Cu^{1+} ions, as well as high optical transparency of around 90%. The highly transparent conducting ZnO and highly resistive ZnO films are under industrial evaluations as transparent electrode in liquid crystal display and components in printed circuit board, respectively.

Preparation of magnetite film and its characteristics

Iron oxide film with a formula of Fe_3O_4 (magnetite) film was prepared by immersing activated substrates into aqueous solution containing iron(III) nitrate hydrous and DMAB at 293-313K.

The film showed characteristic magnetic properties of 480emu/cc in saturation magnetization and 150Oe in coercive force, as shown in Fig.1, and had very smooth surface. The film showed resistivity as high as $2.9x10^{3}\Omega$cm, which was higher by about six orders in magnitudes than that for bulk value.

In summary, the electrochemical process using a nitrate reduction reaction is less hazardous and more environmentally friendly, and will be appropriate for preparing semiconducting and magnetic oxide films industrially employed.

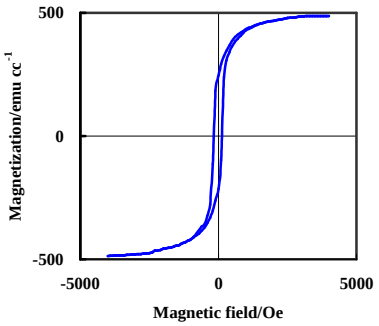

Fig. 1 Magnetization curve for Fe3O4 film.

Reference

1)M. Izaki, et al., Appl. Phys. Lett, 68, 2439 (1996).
2)M. Izaki, et al., J. Electrochem. Soc., 144, L3(1997).
3)M. Izaki, et al., ibid 144, 1949(1997).
4)M. Izaki, ibid, 146, 4517(1999).
5)M. Izaki, et. al, ibid, 147, 210(2000).
6)M. Izaki, Electrochem. Solid. State Lett., 1, 215(1998).
7)M. Izaki, et al, Electrochem. Solid. State Lett., 3, 501(2000).
8)M. Izaki, et al, ADVANCED MATERIALS, 13, 142(2001).